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Al₂O₃ PRODUCED BY THE SOL-GEL METHOD FOR MICROCOMPOSITE CERAMICS

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The possibility of production of Al₂O₃ with a microcomposite structure and microplastic properties from sol-gel compositions at room temperatures is considered. It is demonstrated that high strength parameters are achieved owing to fluidity sites. The Al₂O₃ obtained from periodic sol-gel solutions can be used as a matrix for microcomposite ceramic material.

The use of microcomposite ceramic materials for industrial purposes is currently increasing. These materials have a number of advantages over traditional ceramics based on Al₂O₃, primarily, microplasticity which makes it possible to develop structural products. Due to the microplasticity, the temperature of the deformation relaxation process decreases.

Nanoceramics and microcomposite ceramics are of special interest in this context. The matrix in these ceramics consists of materials with high mobility of the units, ensuring microplasticity at sufficiently low temperatures. The literature sources describe the compositions and dimensions of nanoceramic inclusions of SiC and TiC [1]. The possibility of predicting the microplasticity of oxide and non-oxide compounds produced by the sol-gel method has been established as well [3].

The purpose of the present study was to produce Al₂O₃ with increased microplasticity at moderate (close to room) temperatures employing the sol-gel method. To do this, the microcomposite structure of Al₂O₃ has been formed by units consisting of structural elements (SE) allowing for shifting, turning, and relaxation of deformations.

The x-ray structural analysis of crystalline α -Al₂O₃ and Al₂O₃ produced by the sol-gel method was performed on a DRON-3 diffractometer in Cu-K α radiation. The intensity distribution of a diffracted beam in the strong reflection region (111) of α -Al₂O₃ was analyzed. The size of the edge of a SE was found from the experimentally obtained values of the interplanar distance of the most closely packed plane with the maximum line intensity d_{\max} using the formula

$$a_{\text{SE}} = d_{\max} N^{1/2} \tau^{1/6} K_s^{1/3},$$

where $N = h^2 + k^2 + l^2$ is the sum of the squares of the indexes of the most closely packed plane; $\tau = 1.628$ is the

golden section number; K_s is the shape coefficient of SE ($K_{\text{cube}} = 1$, $K_{\text{octahedron}} = 0.4714$, $K_{\text{tetrahedron}} = 0.1179$).

Sol-gel synthesis of Al₂O₃ was carried out in accordance with the proton-hydration procedure, preventing precipitation of hydrate precipitates. This was achieved by structuring of the sol-gel solutions and control of the size of the SE-based octahedrally shaped units with an edge size of $a_{\text{SE}} = 6.13$ E in the gel-solid transition.

On dissolution of Al(*i*-OC₃H₇)₃ in alcohol-aqueous solution of *i*-C₃H₇OH containing an equimolar amount of H₂O at pH = 7.5, the formation of mononuclear solvated complexes occurs; cation hydration with attendant hydrolysis of organic OR ligands and separation of HOR molecules takes place; formation of stable solutions with subsequent polycondensation of mononuclear complexes and emergence of polymer chains is achieved. As soon as the products of hydrolysis of the linear chains comprise a critical mass, they are condensed in polymer hexagonal rings.

The sol-gel transition is related to an increase in the interaction of bridge and non-bridge OH-groups in the coordination sphere of Al. The reactions which result in the formation of structures with three bonds for bridge oxygen and six bonds for Al become the most efficient from the point of view of thermodynamics. The sol-gel phase is completed with the formation of a stable periodic colloidal structure

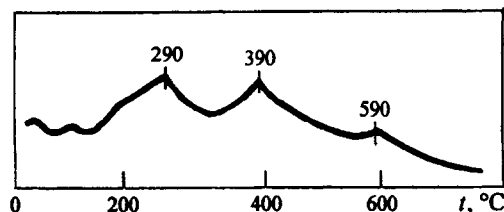


Fig. 1. DTA curve of the products of hydrolytic polycondensation of Al(*i*-OC₃H₇)₃ at pH = 7.5.

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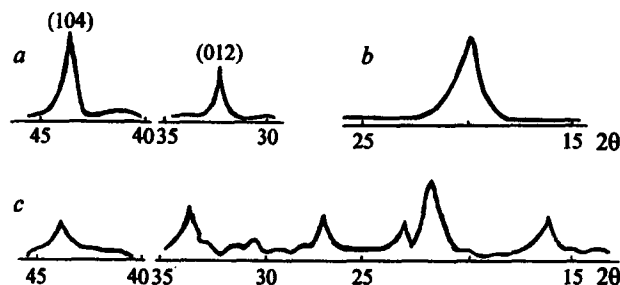


Fig. 2. Diffraction patterns of crystalline α -Al₂O₃ (a) and the products of hydrolytic polycondensation of Al(*i*-OC₂H₅)₃ annealed at the temperature of 100°C for 1 h (b) and at the temperature of 590°C for 3 h (c).

formed by SE of different sizes associated in units. For the defined parameters of the colloidal structure, proton-bearing channels of low activation transfer and mobility typical of the microcomposite structure of solids arise between the ES units. The differential thermal analysis of the gel obtained in the experiment indicated the presence of exothermic peaks at 290, 390, and 590°C (Fig. 1)

Slow removal of the solvent from the gel and subsequent annealing at the temperature of 390°C result in the formation of octahedron-shaped units with an edge size found by x-ray analysis equal to 31.5 E, and distance $R_{O-O} = 15.7$ E for the emerging O – O bonds. At the temperature of 450°C, a structure consisting of SE blocks with $a = 18.9$ E is formed. Finally, a structure consisting of SE blocks with $a = 12.6$ E is formed at the temperature of 590°C with an α -AlOOH \rightarrow α -Al₂O₃ transition. Further holding at the temperature of 590°C is accompanied by the separation of maximum electron density bands similar to the structural elements in crystalline α -Al₂O₃ (Fig. 2). The duplication of the minimum scattering volume is related to the high content of SE blocks.

The mechanical compression tests of the obtained samples of Al₂O₃ were performed on an INSTRON-1185 unit. Figure 3 shows the time dependences of loading (compression) of natural ruby samples and samples produced by the sol-gel method. The high strength parameters of the Al₂O₃ obtained by the sol-gel method are provided by numerous

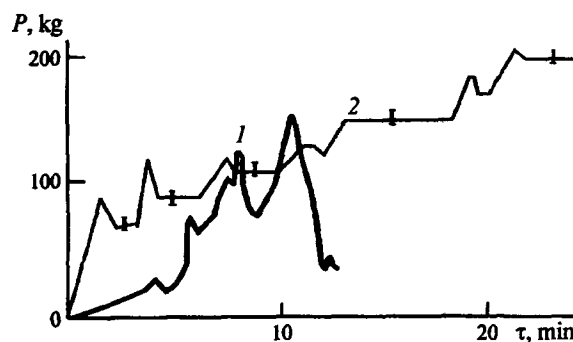


Fig. 3. Loading curves of Al₂O₃ produced by the sol-gel method (1) and natural ruby (2).

fluidity sites. These sites are closely related to the behaviour of the SE blocks, their low-activation shifts and turns. At each deformation level, SE blocks of a certain size are turned. The high mobility of SE blocks, in turn, produces a decrease in the temperature of the gel – Al₂O₃ transition. This nature of deformation relaxation proceeds from the microcomposite structure of corundum. Thus, the possibility of controlling the growth of a structure in the stage of a colloidal solution is confirmed experimentally.

The Al₂O₃ obtained from sol-gel periodic solutions possesses all of the properties typical of microcomposite structures and can be used as a matrix in microcomposite ceramics, as well as in protective and dielectric coatings with controlled thickness.

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